Molecular Modeling of Interactions in Electronic Nose Sensors for Environmental Monitoring

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We report a study aimed at understanding analyte interactions with sensors made from polymer-carbon black composite films. The sensors are used in an Electronic Nose (ENose) which is used for monitoring the breathing air quality in human habitats. The model mimics the experimental conditions of the composite film deposition and formation and was developed using molecular modeling and simulation tools. The Dreiding 2.21 Force Field was used for the polymer and analyte molecules while graphite parameters were assigned to the carbon black atoms. The polymer considered for this work is methyl vinyl ether / maleic acid copolymer. The target analytes include both inorganic (NH_3) and organic (methanol) types of compound. Results indicate different composite-analyte interaction behavior.

Key Words: Electronic Nose, Polymer composite, Environmental monitoring, Molecular modeling, Interactions

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1. Introduction

Monitoring breathing air quality in human habitats in which air is recycled is important to NASA. The availability of a miniature, portable instrument capable of identifying contaminants in the breathing environment at parts-per-million levels would greatly enhance the capability for monitoring the quality of recycled air as well as providing notification of the presence of potentially dangerous substances from spills and leaks. At present, air quality on Space Shuttle flights is determined by collecting samples and analyzing them on the ground using laboratory analytical instruments such as a gas chromatography-mass spectrometer (GC-MS). To fill this need, JPL is developing an Electronic Nose (ENose) for air quality monitoring [1-3].

An electronic nose is an array of chemical sensors, which respond when exposed to vapors. Each sensor is non-specific to any one vapor. Upon exposure to a vapor, the sensors respond, creating a pattern across the array. The Electronic Nose (ENose) developed at JPL uses an array of polymer-carbon black composite sensing films [1-3]. Conductivity is imparted to the polymer film by adding carbon black (CB). The swelling of the polymer matrix upon exposure to organic vapors, results in the breaking of some of the carbon black conductive networks and hence causing a change in the sensor response [1-12].

The underlying objective of this work is to develop molecular models that accurately describe the polymer-carbon black composite films used in the ENose sensors and gain a detailed understanding of polymer composite-analyte interactions. Polymer considered for this work include methyl vinyl ether / maleic acid copolymer. The target analytes include both inorganic (NH_3) and organic (methanol) types of compounds. A combination of molecular simulation tools (molecular mechanics and dynamics) is used to obtain the composite model and also to evaluate its interaction with analytes.

2. Model Development

The molecular simulations were performed on a Silicon Graphics O2 workstation, using the commercial software Cerius^2 [12]. The polymer model is based on its stereisomerism (tacticity) and sequence isomerism (connectivity). The CB in the present work is modeled as naphthalene rings (i.e., small graphite sheets) with no hydrogen as it is difficult to insert large graphite sheets in a high-density

polymer matrix. The Dreiding 2.21 Force Field [13] was used for the polymer and analyte molecules while the graphite parameters were assigned to the carbon black atoms [14]. The model for the polymer-CB composite film is being developed by adopting a strategy that involves performing simulations first under "no solvent" and then under "solvent" conditions mimicking the film casting and formation in the laboratory [15]

The composite model is initially developed under no-solvent conditions (or vacuum). To begin with, the density of the polymer-CB composite film (ρ) is approximated as a linear combination of the sum of bulk density of individual components times their weight fractions, i.e., $\rho = \rho_p x_p + \rho_{cb} x_{cb}$ (where, ρ_p = polymer density, ρ_{cb} = carbon black density, x_p=weight fraction of the polymer and x_{cb}=weight fraction of the carbon black). The densities of the different polymers and CB and used in the current study are listed in Table 1. The JPL ENose films are made with polymer weight fraction of 0.75-0.8 [1-3]. A value of x_p =0.75 was considered for the current composite model development. An amorphous polymer unit cell was built with a density $\rho_p x_p$ and the naphthalene rings were then inserted in the polymer matrix until the composite film density ρ was reached. The entire system is then equilibrated by a combination of molecular mechanics (MM) and dynamics (NVT-MD) simulations at 300 K.

The composite structure obtained under "no solvent conditions" is then subjected to solvent conditions. The composite structure obtained from the previous step is immersed in a large solvent box. This step is done to mimic the polymer-carbon black solution, which is used in solvent casting of the sensor films. The entire system (composite+solvent) is then equilibrated by MM followed by NVT-MD simulations at 300 K.

On reaching equilibrium, the solvent molecules are removed (this step corresponds to deposition of the film and evaporation of the solvent from the sensor film, as done under experimental conditions) and the box is compressed to the target density ρ, followed by density and structural relaxation using NPT-MD and NVT-MD simulations at 300 K, respectively to achieve the final equilibrium structure and density.

3. Results and Discussion

The final composite structure for methyl vinyl ether / maleic acid copolymer at carbon black loading of 25 wt% is shown in Figure 1. This is obtained after removing the solvent, recompressing the box to the initial density and equilibrating it is using NPT-MD and NVT-MD techniques at 300 K. The carbon black clusters are shown as spheres and the polymer chains are shown in cylindrical representation.

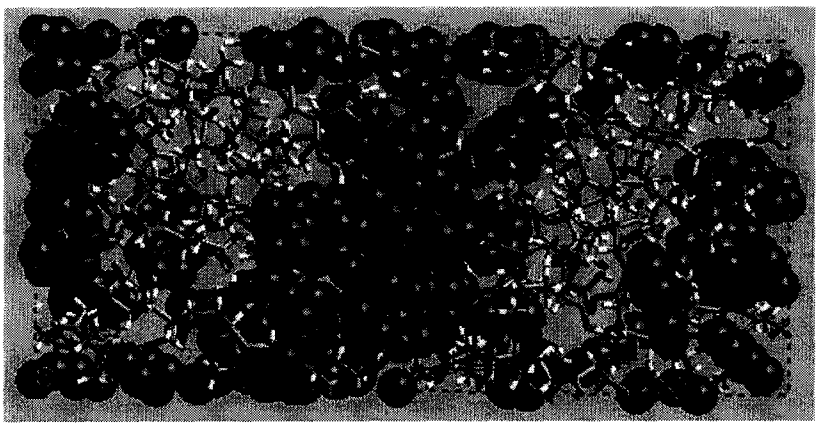

Figure 1: Structure of polymer-carbon black composite model for methyl vinyl ether / maleic acid copolymer

The pressure for the NPT simulations is set to atmospheric pressure. Figure 2 shows the density versus time plots of the composite after performing NPT-MD simulations at 300 K for the final structure. This plot shows the density of the final composite model.

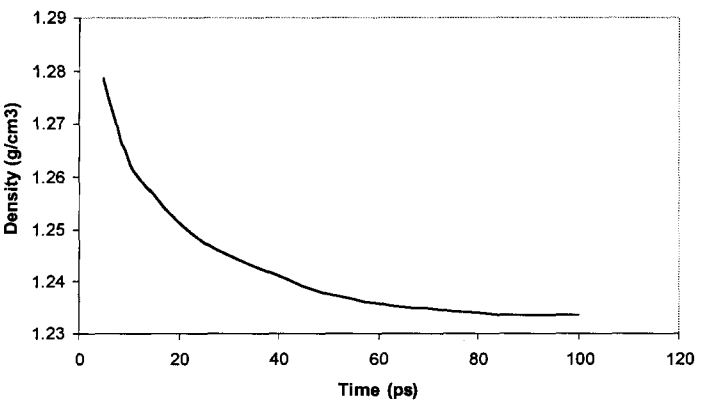

Figure 2: Density versus time plots of the composite obtained by NPT-MD equilibration after solvent removal.

The Spacecraft Maximum Allowable Concentration (SMAC) is the maximum concentration of an analyte permissible aboard an inhabited spacecraft [16]. The SMAC values of the analytes considered for the present study are shown in Table 1.

Table 1: Spacecraft Maximum Allowable Concentration (SMAC) values for the target analytes [16]

Analyte	*SMAC (ppm) 24 hr*
Ammonia	20
Methanol	10

For most compounds, these concentrations are in the single to tens of parts-per-million (ppm) range. It is difficult to perform sorption simulation studies at such low partial pressures of the analyte using the software (experiments being performed at atmospheric pressure) and could lead to no molecules being inserted into the system. So as to investigate the sensor response at low concentrations we decided to carry out the simulations at a fixed analyte loading.

The simulations at a fixed loading of one analyte and at 300 K were performed using the SORPTION module in the Cerius^2 software. The interaction energy of the polymer composite with NH_3 and methanol is shown in Figure 3. It can be seen from the figure that the composite-analyte interaction is stronger for the methanol than for the ammonia. These interaction energies are calculated by considering the composite model containing no analyte as reference.

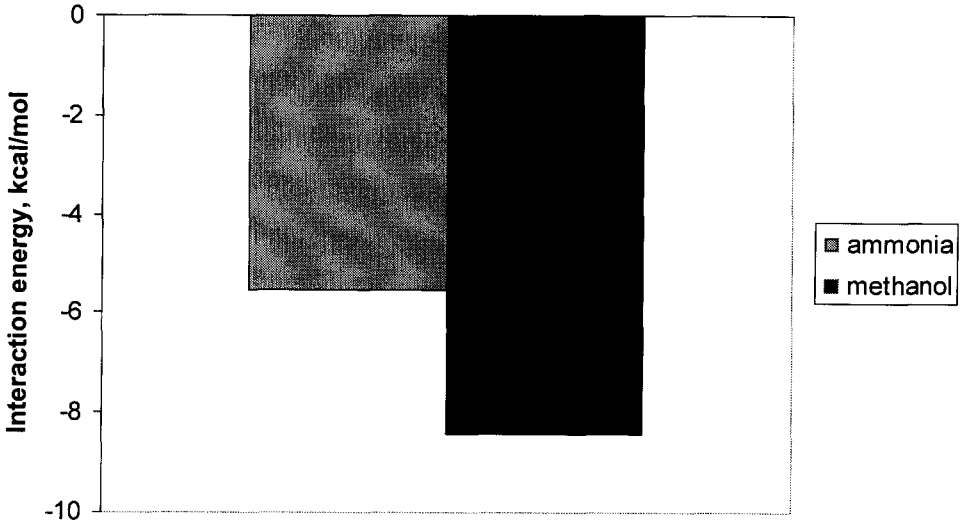

Figure 3: Polymer composite–analyte interaction energy for ammonia and methanol.

4. Conclusions

A molecular model for the polymer composite was developed by an approach that mimics the experimental composite film casting and formation. The composite model consisted of carbon black modeled as naphthalene rings (with no hydrogens) inserted in an amorphous polymer matrix. The sorption studies at fixed analyte loading also predict different composite-analyte interactions.

Acknowledgements

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